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(54) Si-CONTAINING GALVANIZED HIGH STRENGTH STEEL SHEET HAVING GOOD CORROSION RESISTANCE AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high Si-containing high strength galvanized steel sheet having good a coating property and an excellent corrosion resistance without requiring new equipments, and its manufacturing method.

SOLUTION: A Zn-Al-Fe alloy plating or a Zn-Al-Mg-Fe alloy plating is formed on the surface of a steel sheet containing 0.4-2.0 wt.% Si which is the oxidized state (SiO₂) in the inner sheet. The inner SiO₂ is produced at the time, the steel sheet is oxidized under atmosphere having 0.9-1.2 fuel/air ratio in the oxidizing zone, and successively is reduced in the reducing zone, under an atmosphere controlled where the Si content (mass %) (CSi), a water partial pressure (PH₂O) and a hydrogen partial pressure (PH₂) satisfy the following inequality. $-0.8 \geq \log(PH_2O/PH_2) \leq 0.5CSi-3$.

CLAIMS

[Claim(s)]

[Claim 1]Content of an internal oxidation thing of SiO₂ forms 3 micrometers or less of layers which are 0.4 to 2.0 mass % in the surface of a steel plate whose content of Si is 0.4 to 2.0 mass % as the 1st layer, moreover -- 0.05 to aluminum:0.5 mass %, seven to Fe:15 mass %, remainder Zn, and inevitable impurities -- corrosion-resistant good Si

content high intensity alloying hot-dip zinc-coated carbon steel sheet making an alloying hot-dip-zincing layer [from] form.

[Claim 2]Content of an internal oxidation thing of SiO_2 forms 3 micrometers or less of layers which are 0.4 to 2.0 mass % in the surface of a steel plate whose content of Si is 0.4 to 2.0 mass % as the 1st layer, moreover -- 0.05 to aluminum:0.5 mass %, 0.05 to Mg:1.0 mass %, seven to Fe:15 mass %, remainder Zn, and inevitable impurities -- corrosion-resistant good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet making an alloying hot-dip-zincing layer [from] form.

[Claim 3]When content of Si gives hot dip zincing to a steel plate which is 0.4 to 2.0 mass %, This steel plate is oxidized in atmosphere of the combustion air ratios 0.9-1.2 in an oxidized zone, After the logarithm $\log(\text{PH}_2\text{O}/\text{PH}_2)$ of moisture pressure in a subsequent reducing zone and hydrogen content pressure returns in atmosphere with which a lower type (1) is filled, aluminum: A manufacturing method of good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet of the corrosion resistance according to claim 1 carrying out hot dip zincing in a galvanization annealing containing 0.05 - 0.25 mass %, and performing alloying treatment at 460-550 **.

$-0.8 \geq \log(\text{PH}_2\text{O}/\text{PH}_2) \leq 0.5$ CSi-3 -- (1)

However, CSi is a Si content (mass %).

[Claim 4]When content of Si gives hot dip zincing to a steel plate which is 0.4 to 2.0 mass %, This steel plate is oxidized in atmosphere of the combustion air ratios 0.9-1.2 in an oxidized zone, After the logarithm $\log(\text{PH}_2\text{O}/\text{PH}_2)$ of moisture pressure in a subsequent reducing zone and hydrogen content pressure returns in atmosphere with which a lower type (1) is filled, aluminum: A manufacturing method of good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet of the corrosion resistance according to claim 2 carrying out hot dip zincing in a galvanization bath containing 0.05 to 0.25 mass %, and Mg:0.05 - 1.0 mass %, and performing alloying treatment at 460-550 **.

$-0.8 \geq \log(\text{PH}_2\text{O}/\text{PH}_2) \leq 0.5$ CSi-3 -- (1)

However, CSi is a Si content (mass %).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]With respect to Si content high intensity alloying hot-dip zinc-coated carbon steel sheet and its manufacturing method, in detail, this invention has the outstanding corrosion resistance and relates to a plating steel plate applicable as a steel plate for cars, various the use for building materials, for example, object.

[0002]

[Description of the Prior Art]An alloying hot-dip zinc-coated carbon steel sheet is one of those which are used best as a corrosion-resistant good plating steel plate. Usually this alloying hot-dip zinc-coated carbon steel sheet is preheated by a clean heating furnace, after degreasing a steel plate, it performs reduction annealing with a reducing furnace for surface defecation and construction material reservation, immerses in a molten zinc bath after that, and after controlling coating weight, it is manufactured by performing alloying treatment. Thus, since it excels in corrosion resistance, plating adhesion, etc., the manufactured plating steel plate is widely used as the steel plate for cars, or a steel plate

for building materials.

[0003]As for a high Si content high intensity steel plate, the defect of plating nature poses a problem among these steel plates. For the improvement of plating nature, after oxidizing so that the thickness of an oxide film may be 400-10000 Å in a clean heating furnace in a steel surface, to JP,55-122865,A, it anneals under the atmosphere containing hydrogen, and the method of plating is indicated. This method controls generation of Si oxide by making an oxidized zone generate a ferric acid-ized film positively, and aims at raising plating adhesion.

[0004]however -- if control of the reducing time of a ferric acid-ized film is difficult in practice by this method and reducing time is too long -- the surface of Si -- concentration being caused, and, since an iron oxide film remains in a steel surface if too short, Poor plating nature cannot be canceled thoroughly and it has the problem that Si oxide generation cannot be controlled thoroughly. In order to solve this problem, in JP,2-38549,A, the method of performing pre plating before annealing is indicated. However, by this method, equipment of pre plating is needed, when there is no installing space, it cannot adopt, and the production cost rise by pre plating equipment installation is not avoided.

[0005]

[Problem(s) to be Solved by the Invention]This invention is made that plating nature is good and should provide the corrosion-resistant outstanding high Si content high intensity alloying hot-dip zinc-coated carbon steel sheet and its manufacturing method, without installing new equipment like pre plating equipment.

[0006]

[Means for Solving the Problem]a result to which this invention persons repeated research wholeheartedly about plating processing of a high intensity steel plate -- the surface of Si, since concentration originates in an outer oxide film of SiO_2 , By controlling reducing atmosphere appropriately and changing SiO_2 into an internal oxidation state, it found out that poor plating nature could be prevented. By forming Zn-aluminum-Fe-alloy plating or Zn-aluminum-Mg-Fe-alloy plating in the surface of Si content high intensity steel plate which changed SiO_2 into an internal oxidation state, it finds out that corrosion-resistant good Si content high intensity hot-dipping steel plate can be obtained, and came to complete this invention.

[0007]That is, the place made into a gist of this invention is as follows.

[0008](1) Content of an internal oxidation thing of SiO_2 forms 3 micrometers or less of layers which are 0.4 to 2.0 mass % in the surface of a steel plate whose content of Si is 0.4 to 2.0 mass % as the 1st layer, moreover -- 0.05 to aluminum:0.5 mass %, seven to Fe:15 mass %, remainder Zn, and inevitable impurities -- corrosion-resistant good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet making an alloying hot-dip-zincing layer [from] form.

[0009](2) Content of an internal oxidation thing of SiO_2 forms 3 micrometers or less of layers which are 0.4 to 2.0 mass % in the surface of a steel plate whose content of Si is 0.4 to 2.0 mass % as the 1st layer, moreover -- 0.05 to aluminum:0.5 mass %, 0.05 to Mg:1.0 mass %, seven to Fe:15 mass %, remainder Zn, and inevitable impurities -- corrosion-resistant good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet making an alloying hot-dip-zincing layer [from] form.

[0010](3) When content of Si gives hot dip zincing to a steel plate which is 0.4 to 2.0

mass %, This steel plate is oxidized in atmosphere of the combustion air ratios 0.9-1.2 in an oxidized zone, After the logarithm $\log(PH_2O/PH_2)$ of moisture pressure in a subsequent reducing zone and hydrogen content pressure returns in atmosphere with which a lower type (1) is filled, aluminum: A manufacturing method of corrosion-resistant good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet given [aforementioned] in (1) paragraph carrying out hot dip zincing in a galvanization bath containing 0.05 - 0.25 mass %, and performing alloying treatment at 460-550 **.

$-0.8 \geq \log(PH_2O/PH_2) \leq -0.5$ CSi-3 -- (1)

However, CSi is a Si content (mass %).

[0011](4) When content of Si gives hot dip zincing to a steel plate which is 0.4 to 2.0 mass %, This steel plate is oxidized in atmosphere of the combustion air ratios 0.9-1.2 in an oxidized zone, After the logarithm $\log(PH_2O/PH_2)$ of moisture pressure in a subsequent reducing zone and hydrogen content pressure returns in atmosphere with which a lower type (1) is filled, aluminum: A manufacturing method of corrosion-resistant good Si content high intensity alloying hot-dip zinc-coated carbon steel sheet given [aforementioned] in (2) paragraphs carrying out hot dip zincing in a galvanization bath containing 0.05 to 0.25 mass %, and Mg:0.05 - 1.0 mass %, and performing alloying treatment at 460-550 **.

$-0.8 \geq \log(PH_2O/PH_2) \leq -0.5$ CSi-3 -- (1)

However, CSi is a Si content (mass %).

[0012]

[Embodiment of the Invention] This invention is explained in detail below.

[0013] First, Si content high intensity alloying hot-dip zinc-coated carbon steel sheet in this invention makes the thing which made the Zn-aluminum-Fe plating layer form on the high intensity steel plate which is 0.4 to 2 mass %, or a Zn-aluminum-Mg-Fe plating layer form [content / of Si].

[0014] The reason which limited aluminum in a Zn-aluminum-Fe plating layer to 0.05 - 0.5 mass % in this invention is for plating adhesion to deteriorate in case of less than 0.05 mass %, when the alloy layer weak against a ferrite interface in which Zn-Fe-alloy-ization progresses too much at the time of alloying treatment progresses too much. Since plating of iron content which a Fe-aluminum-Zn system barrier layer is thickly formed too much, and alloying does not follow at the time of alloying treatment, but is made into the purpose was not obtained when 0.5 mass % was exceeded, the maximum was made into 0.5 mass %.

[0015] The reason which limited Fe in a Zn-aluminum-Fe plating layer to 7 - 15 mass %, It is for forming soft Zn-Fe alloy in the plating surface, and degrading press-forming nature in case of less than 7 mass %, and is for plating adhesion to deteriorate, when an alloy layer weak against a ferrite interface progresses too much if 15 mass % is exceeded.

[0016] Next, the reason which limited aluminum in a Zn-aluminum-Mg-Fe plating layer to 0.05 - 0.5 mass % in this invention is for plating adhesion to deteriorate in case of less than 0.05 mass %, when the alloy layer weak against a ferrite interface in which Zn-Fe-alloy-ization progresses too much at the time of alloying treatment progresses too much. Since plating of iron content which a Fe-aluminum-Zn system barrier layer is thickly formed too much, and alloying does not follow at the time of alloying treatment, but is made into the purpose was not obtained when 0.5 mass % was exceeded, the maximum was made into 0.5 mass %.

[0017]The reason which limited Mg in a Zn-aluminum-Mg-Fe plating layer to 0.05 - 1 mass % is because the yield of the dross under plating bath will increase substantially and operation will become difficult industrially by less than 0.05 mass %, if improvement in the rust-proof nature of a paint scratch is not found but 1 mass % is exceeded.

[0018]The reason which limited Fe in a Zn-aluminum-Fe plating layer to 7 - 15 mass %, It is for forming soft Zn-Fe alloy in the plating surface, and degrading press-forming nature in case of less than 7 mass %, and is for plating adhesion to deteriorate, when an alloy layer weak against a ferrite interface progresses too much if 15 mass % is exceeded.

[0019]In Si content high intensity alloying hot-dip zinc-coated carbon steel sheet by this invention, The reason which limited the layer whose content of the internal oxidation thing of SiO_2 is 0.4 to 2.0 mass % to 3 micrometers or less between the high intensity steel plate and the plating layer is for the layer containing the internal oxidation thing of SiO_2 to become weak, and for a plating layer to exfoliate easily, if it exceeds 3 micrometers.

[0020]The cause that plating is poor is an Si oxide generated to a steel sheet surface within the reducing zone under annealing. In this invention, the reason which limited Si content C_{Si} in steel to 0.4 - 2.0 mass %, The Si concentration in steel which can control generation of Si oxide by this invention is a range below 2.0 mass %, and is because it cannot have intensity with the sufficient steel plate itself if Si concentration becomes less than 0.4 mass %.

[0021]In order for this invention to perform hot dip zincing to a high intensity steel plate, the oxidized zone in a continuous system hot-dipping line is made to generate a thousands of A ferric acid-ized film first. Since Si is not spread easily in the inside of a ferric acid-ized film, thereby, generation of Si oxide is controlled. However, the combustion air ratio of the oxidized zone at the time of making a ferric acid-ized film form is [0.9 or more] required in order to make enough ferric acid-ized films to control formation of Si oxide generate, and the case of less than 0.9 cannot form enough ferric acid-ized films. Since the ferric acid-ized thickness formed within an oxidized zone will be too thick that it stops to be unable to return within the following reducing zone and a plating bath and an oxide film layer will remain under a plating layer if a combustion air ratio exceeds 1.2, plating adhesion will be checked. Therefore, it is necessary to control the combustion air ratio of an oxidized zone in the range of 0.9-1.2.

[0022]Next, in a reducing zone, it is necessary to return under the atmosphere with which the logarithm $\log(\text{PH}_2\text{O}/\text{PH}_2)$ of moisture pressure and hydrogen content pressure fills a lower type (1). In a reducing zone, N_2 gas which contains H_2 in the range of 1 - 70 mass % is used. Moisture pressure and hydrogen content pressure ($\text{PH}_2\text{O}/\text{PH}_2$) are controlled by introducing a steam in a furnace.

[0023]The reason for having made $\log(\text{PH}_2\text{O}/\text{PH}_2)$ less than -0.8 is because the oxide film of the iron generated with the oxidized zone cannot be returned if -0.8 is exceeded. On the other hand, the reason for having made $\log(\text{PH}_2\text{O}/\text{PH}_2)$ more than 0.5C_{Si}-3 is for external oxidation of Si taking place, and forming the outer oxide film of SiO_2 in a steel sheet surface, and causing poor plating less than [0.5C_{Si}-3]. Namely, the reducing zone needs to return an iron oxide film and needs to make it the atmosphere which changes SiO_2 into an internal oxidation state. Here, the internal oxidation of Si is a phenomenon in which the oxygen diffused in the steel plate reacts to Si near the surface of an alloy, and deposits an oxide. When the diffusion rate to the inner direction of oxygen is far

quicker than the diffusion rate to a way outside Si, an internal oxidation phenomenon has the comparatively high oxygen potential in atmosphere, or when the concentration of Si is low, it happens. Si to the steel sheet surface which is the cause that plating is poor in order for Si to hardly move at this time but to oxidize on that spot -- concentration can be prevented.

[0024]The minimum of aluminum under plating bath was made into 0.05 mass % because the alloy layer weak against a ferrite interface at the time of alloying treatment in which Zn-Fe-alloy-ization progresses too much would progress too much and plating adhesion would deteriorate, if it is less than [this]. The maximum of aluminum was made into 0.25 mass %, in order that a Fe-aluminum-Zn system barrier layer might be easy to be formed at the time of plating and alloying might not progress at the time of alloying treatment, if 0.25 mass % was exceeded.

[0025]When making Mg contain further during a plating bath, the minimum of Mg was made into 0.05 mass % because the effect that the rust-proof nature of a paint scratch improves with an alloying facilitatory effect was also accepted. The maximum was made into 1 mass % in order for the yield of the dross under plating bath to increase substantially and to worsen operability remarkably, if this is exceeded.

[0026]Even if nickel, Sb, Pb, Fe, etc. which are usually added as a trace element are included during the plating bath used by this invention, there is no influence in particular in the effect of this invention.

[0027]As for alloying treatment temperature, it is optimal to carry out in 460-550 **. At less than 460 **, if it is hard to follow alloying and exceeds 550 **, alloying will progress too much, a ferrite interface alloy layer will progress too much, and plating adhesion will deteriorate. Although not set in particular about alloying time, it is decided by balance with alloying temperature, and the range for 10 to 40 seconds is usually suitable on actual operation. Although not set in particular about plating coating weight, more than 10 g/m² from a corrosion-resistant viewpoint is preferred, and it is desirable from a viewpoint of processability that it is below 150 g/m². As an Si content steel intensity steel plate of a ground, this invention is applicable also to the high-tensile steel sheet which will carry out hot rolled sheet steel and cold rolled sheet steel and which was made and added further Ti of the usual super-low carbon system, Nb, B, etc.

[0028]

[Embodiment of the Invention]Based on an example, this invention is explained concretely below.

[0029](Example 1) Plating processing which anneals with the pretreating furnace of a continuous system hot-dip-zincing line, and shows the test specimen shown in Table 1 in Table 2 was performed. The combustion air ratio of the oxidized zone of this pretreating furnace was adjusted to 0.95, and the reducing zone was adjusted so that a steam might be introduced into the nitrogen gas 10 mass % Containing hydrogen and the logarithm $\log (PH_2O/PH_2)$ of moisture pressure and hydrogen content pressure might be set to -1 - - 3.

[0030]

[Table 1]

鋼板 記号	鋼板 種類	化学成分 (mass%)									備考
		C	Si	Mn	P	S	Al	Ti	Nb		
鋼板 A	冷延鋼板	0.0018	0.02	0.04	0.016	0.008	0.038	0.003	0.004	Siが本発明範囲外	
鋼板 B	冷延鋼板	0.072	0.4	0.82	0.01	0.006	0.071	0.052	-		
鋼板 C	冷延鋼板	0.005	0.85	0.74	0.012	0.019	0.075	0.058	0.016		
鋼板 D	冷延鋼板	0.02	1.62	1.81	0.005	0.003	0.048	0.034	-		
鋼板 E	冷延鋼板	0.064	1.83	2.35	0.004	0.005	0.063	0.018	0.017		
鋼板 F	熱延鋼板	0.077	1.47	1.69	0.011	0.002	0.054	0.002	-		

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[0031]

[Table 2]

番 号	鋼板 記号	酸化物 燃焼空気比	還元率 log(PH ₂ /P _{H₂O})	めっき厚 (mass%)	Al	Mg	Fe	内部酸化物 厚さ	めっき 密着性	T S	備 考
1	鋼板 A	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	比較例	
2	鋼板 A	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	比較例	
3	鋼板 B	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	本発明例	
4	鋼板 B	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	本発明例	
5	鋼板 B	0.95	-1~ -3	0.25	0.5	10	1 μm	合格	合格	本発明例	
6	鋼板 B	0.95	-1~ -3	0.25	—	10	1 μm	合格	合格	本発明例	
7	鋼板 C	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	本発明例	
8	鋼板 C	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	本発明例	
9	鋼板 C	0.95	-1~ -3	0.25	0.5	10	1 μm	合格	合格	本発明例	
10	鋼板 C	0.95	-1~ -3	0.25	—	10	1 μm	合格	合格	本発明例	
11	鋼板 D	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	本発明例	
12	鋼板 D	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	本発明例	
13	鋼板 D	0.95	-1~ -3	0.25	0.5	10	1 μm	合格	合格	本発明例	
14	鋼板 D	0.95	-1~ -3	0.25	—	10	1 μm	合格	合格	本発明例	
15	鋼板 D	0.95	-1~ -3	0.25	0.5	10	3 μm	合格	合格	本発明例	
16	鋼板 D	0.95	-1~ -3	0.25	—	10	3 μm	合格	合格	本発明例	
17	鋼板 D	0.95	-1~ -3	0.25	0.5	10	5 μm	不合格	合格	比較例	
18	鋼板 D	0.95	-1~ -3	0.25	—	10	5 μm	不合格	合格	比較例	
19	鋼板 E	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	本発明例	
20	鋼板 E	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	本発明例	
21	鋼板 E	0.95	-1~ -3	0.25	0.5	10	1 μm	合格	合格	本発明例	
22	鋼板 E	0.95	-1~ -3	0.25	—	10	1 μm	合格	合格	本発明例	
23	鋼板 E	0.95	-1~ -3	0.25	0.5	10	3 μm	合格	合格	本発明例	
24	鋼板 E	0.95	-1~ -3	0.25	—	10	3 μm	合格	合格	本発明例	
25	鋼板 E	0.95	-1~ -3	0.25	0.5	10	5 μm	不合格	合格	比較例	
26	鋼板 E	0.95	-1~ -3	0.25	—	10	5 μm	不合格	合格	比較例	
27	鋼板 F	0.95	-1~ -3	0.25	0.5	10	0 μm	合格	合格	本発明例	
28	鋼板 F	0.95	-1~ -3	0.25	—	10	0 μm	合格	合格	本発明例	
29	鋼板 F	0.95	-1~ -3	0.25	0.5	10	1 μm	合格	合格	本発明例	
30	鋼板 F	0.95	-1~ -3	0.25	—	10	1 μm	合格	合格	本発明例	
31	鋼板 F	0.95	-1~ -3	0.25	0.5	10	3 μm	合格	合格	本発明例	
32	鋼板 F	0.95	-1~ -3	0.25	—	10	3 μm	合格	合格	本発明例	
33	鋼板 F	0.95	-1~ -3	0.25	0.5	10	5 μm	不合格	合格	比較例	
34	鋼板 F	0.95	-1~ -3	0.25	—	10	5 μm	不合格	合格	比較例	

下線付きは本発明範囲外

[0032] Hot dip zincing contains 460 ** of plating bath temperature, and aluminum, or plated them with the hot-dip-zincing bath containing aluminum and Mg, and adjusted plating coating weight to 60 g/m² by nitrogen gas wiping. Then, the plating adhesion of the plating steel plate obtained by performing alloying treatment with a 460-550 ** alloying furnace was evaluated.

[0033] Plating adhesion inspected powdering and made the rejection the case where the exfoliation width was set to more than 3 mm. The strength test of the steel plate was done

according to JIS Z 2201, and considered tensile strength of 350 or more MPa as success. An evaluation result is shown in Table 2.

[0034]As for the numbers 1 and 2, since the Si content of the steel plate A was outside the range of this invention, intensity became a rejection. Internal oxidation layer thickness became the outside of this invention range, and the numbers 17, 18, 25, 26, 33, and 34 are the examples which are inferior in plating adhesion, and all brought a result with good plating adhesion and intensity except these.

[0035](Example 2) Plating processing which anneals with the pretreating furnace of a continuous system hot-dip-zincing line, and shows the test specimen shown in Table 1 in Table 3 was performed. The combustion air ratio of the oxidized zone of this pretreating furnace was adjusted to 1.05, and the reducing zone was adjusted so that a steam might be introduced into the nitrogen gas 10 mass % Containing hydrogen and the logarithm $\log (PH_2O/PH_2)$ of moisture pressure and hydrogen content pressure might be set to -1.2.

[0036]

[Table 3]

試 号	鋼板 型号	酸化率 酸濃度比	還元率 log (P40/P4)	約つき厚 (mass%) Al Fe	プレス 成形性	めっき 密着性	T S	備 考
1	鋼板 A	1.05	-1.2	0.25	8	合格	合格	不合格 比較例
2	鋼板 A	1.05	-1.2	0.25	10	合格	合格	不合格 比較例
3	鋼板 A	1.05	-1.2	0.25	12	合格	合格	不合格 比較例
4	鋼板 B	1.05	-1.2	0.25	6	不合格	合格	合格 比較例
5	鋼板 B	1.05	-1.2	0.25	7	合格	合格	合格 本発明例
6	鋼板 B	1.05	-1.2	0.25	10	合格	合格	合格 本発明例
7	鋼板 B	1.05	-1.2	0.25	15	合格	合格	合格 本発明例
8	鋼板 B	1.05	-1.2	0.25	17	合格	合格	合格 比較例
9	鋼板 B	1.05	-1.2	0.03	15	合格	合格	合格 比較例
10	鋼板 B	1.05	-1.2	0.1	10	合格	合格	合格 本発明例
11	鋼板 B	1.05	-1.2	0.5	8	合格	合格	合格 本発明例
12	鋼板 B	1.05	-1.2	0.6	5	不合格	合格	合格 比較例
13	鋼板 C	1.05	-1.2	0.25	6	不合格	合格	合格 比較例
14	鋼板 C	1.05	-1.2	0.25	7	合格	合格	合格 本発明例
15	鋼板 C	1.05	-1.2	0.25	10	合格	合格	合格 本発明例
16	鋼板 C	1.05	-1.2	0.25	15	合格	合格	合格 本発明例
17	鋼板 C	1.05	-1.2	0.25	17	合格	合格	合格 比較例
18	鋼板 C	1.05	-1.2	0.03	15	合格	合格	合格 比較例
19	鋼板 C	1.05	-1.2	0.1	10	合格	合格	合格 本発明例
20	鋼板 C	1.05	-1.2	0.5	8	合格	合格	合格 本発明例
21	鋼板 C	1.05	-1.2	0.6	5	不合格	合格	合格 比較例
22	鋼板 D	1.05	-1.2	0.25	6	不合格	合格	合格 比較例
23	鋼板 D	1.05	-1.2	0.25	7	合格	合格	合格 本発明例
24	鋼板 D	1.05	-1.2	0.25	10	合格	合格	合格 本発明例
25	鋼板 D	1.05	-1.2	0.25	15	合格	合格	合格 本発明例
26	鋼板 D	1.05	-1.2	0.25	17	合格	合格	合格 比較例
27	鋼板 D	1.05	-1.2	0.03	15	合格	合格	合格 比較例
28	鋼板 D	1.05	-1.2	0.1	10	合格	合格	合格 本発明例
29	鋼板 D	1.05	-1.2	0.5	8	合格	合格	合格 本発明例
30	鋼板 D	1.05	-1.2	0.6	5	不合格	合格	合格 比較例
31	鋼板 E	1.05	-1.2	0.25	6	不合格	合格	合格 比較例
32	鋼板 E	1.05	-1.2	0.25	7	合格	合格	合格 本発明例
33	鋼板 E	1.05	-1.2	0.25	10	合格	合格	合格 本発明例
34	鋼板 E	1.05	-1.2	0.25	15	合格	合格	合格 本発明例
35	鋼板 E	1.05	-1.2	0.25	17	合格	合格	合格 比較例
36	鋼板 E	1.05	-1.2	0.03	15	合格	合格	合格 比較例
37	鋼板 E	1.05	-1.2	0.1	10	合格	合格	合格 本発明例
38	鋼板 E	1.05	-1.2	0.5	8	合格	合格	合格 本発明例
39	鋼板 E	1.05	-1.2	0.6	5	不合格	合格	合格 比較例
40	鋼板 F	1.05	-1.2	0.25	6	不合格	合格	合格 比較例
41	鋼板 F	1.05	-1.2	0.25	7	合格	合格	合格 本発明例
42	鋼板 F	1.05	-1.2	0.25	10	合格	合格	合格 本発明例
43	鋼板 F	1.05	-1.2	0.25	15	合格	合格	合格 本発明例
44	鋼板 F	1.05	-1.2	0.25	17	合格	合格	合格 比較例
45	鋼板 F	1.05	-1.2	0.03	15	合格	合格	合格 比較例
46	鋼板 F	1.05	-1.2	0.1	10	合格	合格	合格 本発明例
47	鋼板 F	1.05	-1.2	0.5	8	合格	合格	合格 本発明例
48	鋼板 F	1.05	-1.2	0.6	5	不合格	合格	合格 比較例

下線付は本発明範囲外

[0037] Hot dip zincing was plated with the hot-dip-zincing bath containing 460 ** of plating bath temperature, and aluminum, and adjusted plating coating weight to 60g/[m]² by nitrogen gas wiping. Then, the press-forming nature and plating adhesion of the plating steel plate which were acquired by performing alloying treatment with a 460-550 ** alloying furnace were evaluated.

[0038] Press-forming nature did the bead drawing examination in order to investigate galling of plating in press working of sheet metal. A test condition is shown below.

** sample drawing width: -- 30 mm** metallic mold: -- one side -- phi4-mm cylinder and an opposite hand -- plate ** pressing load:500kg** drawing speed:200 mm/min** oiling:slushing oil spreading [0039] Evaluation of press-forming nature made the rejection what galling generated and the specimen fractured, and considered what was able to be

drawn out as success. Plating adhesion inspected powdering nature and made the rejection the case where the exfoliation width was set to more than 3 mm. Intensity of the steel plate was performed according to JIS Z 2201, and considered tensile strength of 350 or more MPa as success. An evaluation result is shown in Table 3.

[0040] Since the Si content of the steel plate A was outside this invention range, intensity was insufficient for the numbers 1-3, and they became a rejection.

[0041] The numbers 4, 13, 22, 31, and 40 are inferior to press-forming nature in the Fe content in a plating layer out of this invention range. The Fe content in a plating layer is [numbers 8, 17, 26, 35, and 44] inferior in plating adhesion out of this invention range.

[0042] The Al content in a plating layer is [numbers 9, 18, 27, 36, and 45] inferior in plating adhesion out of this invention range. The numbers 12, 21, 30, 39, and 48 are inferior to press-forming nature in the Al content and the Fe content in a plating layer out of this invention range.

[0043] Each brought a result with good press-forming nature, plating adhesion, and intensity except these.

[0044] (Example 3) Plating processing which anneals with the pretreating furnace of a continuous system hot-dip-zincing line, and shows the test specimen shown in Table 1 in Table 4 was performed. The combustion air ratio of the oxidized zone of this pretreating furnace was adjusted to 1.05, and the reducing zone was adjusted so that a steam might be introduced into the nitrogen gas 10 mass % Containing hydrogen and the logarithm $\log (PH_2O/PH_2)$ of moisture pressure and hydrogen content pressure might be set to -1.2.

[0045]

[Table 4]

鋼板 記号	酸化率 酸素当量比	還元率 $\log (PH_2O/PH_2)$	めっき層 Al	めっき層 Mg	めっき層 Fe	プレス 成形性	めっき 密着性	耐食性	T S	備 考
1 鋼板 A	1.05	-1.2	0.25	0.5	10	合格	合格	◎	不合格	比較例
2 鋼板 B	1.05	-1.2	0.25	-	10	合格	合格	△	合格	本発明例
3 鋼板 B	1.05	-1.2	0.25	0.33	10	合格	合格	○	合格	本発明例
4 鋼板 B	1.05	-1.2	0.25	0.1	10	合格	合格	◎	合格	本発明例
5 鋼板 B	1.05	-1.2	0.25	0.5	10	合格	合格	◎	合格	本発明例
6 鋼板 B	1.05	-1.2	0.25	1	10	合格	合格	◎	合格	本発明例
7 鋼板 C	1.05	-1.2	0.25	-	10	合格	合格	△	合格	本発明例
8 鋼板 C	1.05	-1.2	0.25	0.33	10	合格	合格	○	合格	本発明例
9 鋼板 C	1.05	-1.2	0.25	0.1	10	合格	合格	◎	合格	本発明例
10 鋼板 C	1.05	-1.2	0.25	0.5	10	合格	合格	◎	合格	本発明例
11 鋼板 C	1.05	-1.2	0.25	1	10	合格	合格	◎	合格	本発明例
12 鋼板 D	1.05	-1.2	0.25	-	10	合格	合格	△	合格	本発明例
13 鋼板 D	1.05	-1.2	0.25	0.33	10	合格	合格	○	合格	本発明例
14 鋼板 D	1.05	-1.2	0.25	0.1	10	合格	合格	◎	合格	本発明例
15 鋼板 D	1.05	-1.2	0.25	0.5	10	合格	合格	◎	合格	本発明例
16 鋼板 D	1.05	-1.2	0.25	1	10	合格	合格	◎	合格	本発明例
17 鋼板 E	1.05	-1.2	0.25	-	10	合格	合格	△	合格	本発明例
18 鋼板 E	1.05	-1.2	0.25	0.33	10	合格	合格	○	合格	本発明例
19 鋼板 E	1.05	-1.2	0.25	0.1	10	合格	合格	◎	合格	本発明例
20 鋼板 E	1.05	-1.2	0.25	0.5	10	合格	合格	◎	合格	本発明例
21 鋼板 E	1.05	-1.2	0.25	1	10	合格	合格	◎	合格	本発明例
22 鋼板 F	1.05	-1.2	0.25	-	10	合格	合格	△	合格	本発明例
23 鋼板 F	1.05	-1.2	0.25	0.33	10	合格	合格	○	合格	本発明例
24 鋼板 F	1.05	-1.2	0.25	0.1	10	合格	合格	◎	合格	本発明例
25 鋼板 F	1.05	-1.2	0.25	0.5	10	合格	合格	◎	合格	本発明例
26 鋼板 F	1.05	-1.2	0.25	1	10	合格	合格	◎	合格	本発明例

下線付字は本発明範囲外

[0046] Hot dip zincing contains 460 ** of plating bath temperature, and aluminum, or plated them with the hot-dip-zincing bath containing aluminum and Mg, and adjusted

plating coating weight to 60 g/m² by nitrogen gas wiping. Then, the press-forming nature and plating adhesion of the plating steel plate which were acquired by performing alloying treatment with a 460-550 °C alloying furnace were evaluated.

[0047] Press-forming nature did the bead drawing examination in order to investigate galling of plating in press working of sheet metal. A test condition is shown below.

** sample drawing width: -- 30 mm** metallic mold: -- one side -- ϕ 4-mm cylinder and an opposite hand -- plate** pressing load: 500 kg** drawing speed: 200 mm/min** oiling: slushing oil spreading [0048] Evaluation of press-forming nature made the rejection what galling generated and the specimen fractured, and considered what was able to be drawn out as success. Plating adhesion inspected powdering nature and made the rejection the case where the exfoliation width was set to more than 3 mm.

[0049] After corrosion resistance prepared the sample which cut to 150x70 mm and performed electropainting for cars, and 20 micrometers of electrostatic coating [80 micrometers of], respectively and gave the cross cut by the cutter, marks attachment which shows the rust generation state after CCT30 cycle below estimated it.

[0050] CCT made one cycle SST2hr-> dry 4hr-> humidity 2hr. Marks considered more than ** as success.

[0051] (Rust generation state)

O : -- less than [not less than 5% of less than 5% of rust generating O: rust generating 10%] ** : -- more than less than [more than rust generating 10% 30%] x: 30%

[0052] Intensity of the steel plate was performed according to JIS Z 2201, and considered tensile strength of 350 or more MPa as success. An evaluation result is shown in Table 4.

[0053] Since the Si content of the steel plate A was outside this invention range, intensity was insufficient for the number 1 and it became a rejection. In this invention, the rust-proof nature of the paint scratch improved by adding Mg in a plating layer.

[0054] (Example 4) The continuous system hot-dipping line was used and plating nature when plated with the conditions shown in Table 5 to cold rolled sheet steel or hot rolled sheet steel was evaluated. When poor plating, such as un-plating, occurred for a product, evaluation of plating nature inspected the powdering nature of the product, and made the rejection the case where the exfoliation width was set to more than 3 mm. After powdering nature stuck the tape on the plating steel plate, it was bent 180 degrees, was returned, stripped the tape, and evaluated the width of plating adhering to a tape as exfoliation width. A result is shown in Table 5.

[0055]

[Table 5]

番号	鋼板種類	酸化帯 燃焼空気比	還元帯 log (PH ₂ O/FH ₂)	鋼板中 Si含有量	めっき溶 (mass%) Al濃度	Fe濃度	評価	備考
1	冷延鋼板	1.05	-1.2	0.4%	0.1	-	合格	本発明例
2	冷延鋼板	1.05	-1.2	0.6%	0.1	-	合格	本発明例
3	冷延鋼板	1.05	-1.2	0.8%	0.1	-	合格	本発明例
4	冷延鋼板	1.05	-1.2	1.5%	0.1	-	合格	本発明例
5	冷延鋼板	1.05	-1.2	2.0%	0.1	-	合格	本発明例
6	冷延鋼板	1.05	-1.2	1.0%	0.1	-	合格	本発明例
7	冷延鋼板	0.8	-1.2	1.0%	0.1	-	不合格	比較例
8	冷延鋼板	0.9	-1.2	1.0%	0.1	-	不合格	比較例
9	冷延鋼板	1	-1.2	1.0%	0.1	-	不合格	比較例
10	冷延鋼板	1.1	-1.2	1.0%	0.1	-	不合格	比較例
11	冷延鋼板	1.2	-1.2	1.0%	0.1	-	不合格	比較例
12	冷延鋼板	1.5	-1.2	1.0%	0.1	-	不合格	比較例
13	冷延鋼板	1.05	-0.6	1.0%	0.1	-	不合格	比較例
14	冷延鋼板	1.05	-0.8	1.0%	0.1	-	合格	本発明例
15	冷延鋼板	1.05	-1.0	1.0%	0.1	-	合格	本発明例
16	冷延鋼板	1.05	-1.5	1.0%	0.1	-	合格	本発明例
17	冷延鋼板	1.05	-2.0	1.0%	0.1	-	合格	本発明例
18	冷延鋼板	1.05	-2.6	1.0%	0.1	-	不合格	比較例
19	冷延鋼板	0.9	-1.2	0.4%	0.1	-	合格	本発明例
20	冷延鋼板	1.2	-1.2	0.4%	0.1	-	合格	本発明例
21	冷延鋼板	1.5	-1.2	0.4%	0.1	-	不合格	比較例
22	冷延鋼板	1.05	-0.6	0.4%	0.1	-	不合格	比較例
23	冷延鋼板	1.05	-0.8	0.4%	0.1	-	合格	本発明例
24	冷延鋼板	1.05	-2.0	0.4%	0.1	-	合格	本発明例
25	冷延鋼板	1.05	-3.0	0.4%	0.1	-	合格	本発明例
26	冷延鋼板	1.05	-3.2	0.4%	0.1	-	不合格	比較例
27	冷延鋼板	0.9	-1.2	2.0%	0.1	-	合格	本発明例
28	冷延鋼板	1.2	-1.2	2.0%	0.1	-	合格	本発明例
29	冷延鋼板	1.5	-1.2	2.0%	0.1	-	不合格	比較例
30	冷延鋼板	1.05	-0.6	2.0%	0.1	-	不合格	比較例
31	冷延鋼板	1.05	-0.8	2.0%	0.1	-	合格	本発明例
32	冷延鋼板	1.05	-2.0	2.0%	0.1	-	合格	本発明例
33	冷延鋼板	1.05	-2.2	2.0%	0.1	-	不合格	比較例
34	冷延鋼板	1.05	-1.2	1.0%	0.02	-	不合格	比較例
35	冷延鋼板	1.05	-1.2	1.0%	0.05	-	合格	本発明例
36	冷延鋼板	1.05	-1.2	1.0%	0.2	-	合格	本発明例
37	冷延鋼板	1.05	-1.2	1.0%	0.25	-	合格	本発明例
38	冷延鋼板	1.05	-1.2	1.0%	0.3	-	不合格	比較例
39	冷延鋼板	1.05	-1.2	1.0%	0.1	0.1	合格	本発明例
40	冷延鋼板	1.05	-1.2	1.0%	0.1	0.5	合格	本発明例
41	冷延鋼板	1.05	-1.2	1.0%	0.1	1	合格	本発明例
42	熱延鋼板	1.05	-1.2	1.0%	0.1	-	合格	本発明例

下線付きは本発明範囲外

[0056] Since the combustion air ratio in an oxidized zone was outside this invention range, enough ferric acid-ized films could not be formed, but un-plating occurred, and the number 7 became a rejection. Since a combustion air ratio was outside this invention range, the numbers 12, 21, and 29 had too thick the ferric acid-ized film, and were inferior in powdering nature.

[0057] Since the logarithm of the moisture pressure in a reducing zone and hydrogen content pressure was outside this invention, a ferric acid-ized film could not be returned enough, but powdering nature deteriorated, and the numbers 13, 22, and 30 became a rejection. Since the logarithm of the moisture pressure in a reducing zone and hydrogen content pressure was outside this invention, the outer oxide film of SiO₂ formed in the steel sheet surface, un-plating occurred, and the numbers 18, 26, and 33 became a

rejection.

[0058] Each showed good plating nature except these.

[0059]

[Effect of the Invention] As stated above, the steel plate in this invention on the surface of Si content high intensity steel plate Zn-aluminum-Fe-alloy plating, Or in manufacturing Si content high intensity alloying hot-dip zinc-coated carbon steel sheet, if the corrosion resistance outstanding by performing Zn-aluminum-Mg-Fe-alloy plating can be acquired and the manufacturing method of this invention is followed, the manufacturing efficiency can be raised remarkably and the industrial meaning is large.